

ENCAPSULATED MATERIALS

FIELD OF THE INVENTION

The present invention is directed to a method for making capsules, and novel capsules containing fragrance materials. The capsules are well suited for use in personal care applications, laundry products and perfume and fragrance products.

BACKGROUND OF THE INVENTION

Encapsulation of fragrance materials is well known in the art. Encapsulation provides advantages to the fragrance product including the protection of the fragrance in the capsule core by a shell until the fragrance is intended to be delivered. In particular, capsules are often designed to deliver their contents at a desired time by the capsule shell being compromised at the desired time.

The capsule shell can be compromised by various factors such as temperature so that the contents are delivered when the capsule begins to melt. Alternatively the capsules can be compromised by physical forces, such as crushing, or other methods that compromise the integrity of the capsule. Additionally, the capsule contents may be delivered via diffusion through the capsule wall during a desired time interval.

It is obviously not desired that the core be released from the shell prematurely. Often, the capsule shell is somewhat permeable to the core contents when stored under certain conditions. This is particularly the case when many capsule types, such as those having aminoplast or cross-linked gelatin walls, are stored in aqueous bases, particularly those containing surfactants. In these cases, although the capsule shell is intact, the fragrance is removed from the core over time in a leaching process. The overall leaching mechanism may be viewed as a diffusion process, with transfer occurring from the

capsule core to the aqueous media, followed by transfer to or solubilization into the surfactant micelles or vesicles. With normal surfactant concentrations of between 4 and 30% in consumer products, as compared to fragrance levels of 0.3 to 1%, it is clear that the partitioning favors absorption by the surfactant over time.

Bases that are primarily non-aqueous in nature, e.g., those that are based on alcohols, or volatile silicones can also leach fragrance from capsules over time. In these product types, the base solvent itself solubilizes the fragrance.

U.S. Patent 6,106,875 discloses a method of encapsulating an amphiphilic volatile flavor or fragrance compound into a microcapsule have a hydrogel shell and an oil core. The flavor or fragrance compound in a liquid is transported into and solubilized into the core using water in the capsule wall to transport the material. The patent discloses that this technique provides a wall thickness and a flavor or fragrance concentration not previously obtainable.

Despite the above teaching and previous encapsulation technologies, there is an ongoing need to develop fragrance systems which are designed to retain the fragrance with minimal losses until it is needed and then be able to deliver the fragrance at the appropriate time.

SUMMARY OF THE INVENTION

It has been discovered that proper capsule core design can reduce and/or slow the effects of leaching of fragrance materials from the core.

One embodiment of the invention is the use of a vast preponderance of fragrance materials with ClogP greater than 3.3, preferably greater than 4. In this embodiment of the invention greater than about 60 weight percent of the fragrance materials have a ClogP of greater than 3.3. In another highly preferred embodiment of the invention more than 80 weight percent of the fragrances have a ClogP value of greater than about 4.0.

Another embodiment is the use of significant levels of appropriate hydrophobic solvents in the fragrance core. Preferably greater than 30% of the core should consist of a hydrophobic solvent, and preferably that solvent should be selected from the group consisting of triglyceride oil, mono and diglycerides, mineral oil, silicone oil, polyalphaolefins, fatty alcohols, diethyl phthalate, and isopropyl myristate.

A third embodiment involves the use of hydrophobic polymers in the core to reduce leaching. Preferably less than about 20% weight percent of polymer is used, and preferably that polymer is selected from the group consisting of ethyl cellulose, hydroxypropyl cellulose, ethylene vinyl acetate, polystyrene, and polyvinyl pyrrolidone and ester terminated polyamides or amide terminated polyamides.

In a fourth embodiment of the invention, since the capsule wall is permeable, it is possible for capsules containing a core of hydrophobic solvent, and/or high ClogP fragrance materials, to actually absorb fragrance materials from a fragrance containing base. This process can be improved via the initial inclusion of a more soluble solvent, which may be a lower ClogP fragrance material, in the core which partitions out of the core when placed in the base, thus providing free volume for fragrance material initially present in the base to occupy.

The migration of fragrance materials into the capsule also provides for the production of capsules by simply loading the capsules into a high concentration of fragrance material. The fragrance materials will preferably migrate into the core of the capsules. This allows an encapsulated fragrance to be manufactured by the selection of a permeable capsule material and hydrophobic core and immersing the capsules in a liquid system that contains a high fragrance loading.

These and other embodiments of the present invention will be set forth in greater detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross sectional drawing of the particle.

Figure 2 is a graph of fragrance release over time versus the measured ClogP of the fragrances.

Figure 3 is a graph of fragrance release over time versus the ClogP of the fragrance in a fabric softener.

DETAILED DESCRIPTION OF THE INVENTION

The logP of many perfume ingredients has been reported, for example, the Ponomarev database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS) Irvine, California. The values are most conveniently calculated using ClogP program also available from Daylight CIS. The program also lists experimentally determined logP values when available from the Ponomarev database. The calculated logP (ClogP) is normally determined by the fragment approach on Hansch and Leo (A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J.B. Taylor and C.A. Ransden, Editors, p. 295 Pergamon Press, 1990). This approach is based upon the chemical structure of the fragrance ingredient and takes into account the numbers and types of atoms, the atom connectivity and chemical bonding. The ClogP values which are most reliable and widely used estimates for this physiochemical property can be used instead of the experimental LogP values useful in the present invention. Further information regarding ClogP and logP values can be found in U.S. Patent 5,500,138.

Fragrance materials with lower logP or ClogP (these terms will be used interchangeably from this point forward) exhibit higher aqueous solubility. Thus, when these materials are in the core of a capsule which is placed in an aqueous system, they will have a greater tendency to diffuse into the base if the shell wall is permeable to the fragrance materials. Without wishing to be bound by theory, it is believed that normally

the mechanism of leaching from the capsule proceeds in three steps in an aqueous base. First, fragrance dissolves into the water that hydrates the shell wall. Second, the dissolved fragrance diffuses through the shell wall into the bulk water phase. Third, the fragrance in the water phase is absorbed by the hydrophobic portions of the surfactant dispersed in the base, thus allowing leaching to continue.

This situation may be improved by one embodiment of the present invention which involves the use of a vast preponderance of high ClogP fragrance materials. In this embodiment of the invention greater than about 60 weight percent of the fragrance materials have a ClogP of greater than 3.3. In another highly preferred embodiment of the invention more than 80 weight percent of the fragrances have a ClogP value of greater than about 4.0. Use of fragrance materials as described previously reduces the diffusion of fragrance through the capsule wall and into the base under specific time, temperature, and concentration conditions.

The following fragrance ingredients provided in Table I are among those suitable for inclusion within the capsule of the present invention:

TABLE I

PERFUME INGREDIENTS	CLOGP
Allyl cyclohexane propionate	3.935
Ambrettolide	6.261
Amyl benzoate	3.417
Amyl cinnamate	3.771
Amyl cinnamic aldehyde	4.324
Amyl cinnamic aldehyde dimethyl acetal	4.033
Iso-amyl salicylate	4.601
Aurantiol (Trade name for Hydroxycitronellal-methylanthranilate)	4.216
Benzyl salicylate	4.383
para-tert-Butyl cyclohexyl acetate	4.019

Iso butyl quinoline	4.193
PERFUME INGREDIENTS	CLOGP
beta-Caryophyllene	6.333
Cadinene	7.346
Cedrol	4.530
Cedryl acetate	5.436
Cedryl formate	5.070
Cinnamyl cinnamate	5.480
Cyclohexyl salicylate	5.265
Cyclamen aldehyde	3.680
Diphenyl methane	4.059
Diphenyl oxide	4.240
Dodecalactone	4.359
Iso E Super (Trade name for 1-(1,2,3,4,5,6,7,8-Octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-ethanone)	3.455
Ethylene brassylate	4.554
Ethyl undecylenate	4.888
Exaltolide (Trade name for 15-Hydroxyentadecanloic acid, lactone)	5.346
Galaxolide (Trade name for 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyran)	5.482
Geranyl anthranilate	4.216
Geranyl phenyl acetate	5.233
Hexadecanolide	6.805
Hexenyl salicylate	4.716
Hexyl cinnamic aldehyde	5.473
Hexyl salicylate	5.260
Alpha-Irone	3.820
Lilial (Trade name for para-tertiary-Butyl-alpha-methyl hydrocinnamic aldehyde)	3.858
Linalyl benzoate	5.233
Methyl dihydrojasnone	4.843
Gamma-n-Methyl ionone	4.309

Musk indanone	5.458
PERFUME INGREDIENTS	CLOGP
Musk tibetine	3.831
Oxahexadecanolide-10	4.336
Oxahexadecanolide-11	4.336
Patchouli alcohol	4.530
Phantolide (Trade name for 5-Acetyl-1,1,2,3,3,6-hexamethyl indan)	5.977
Phenyl ethyl benzoate	4.058
Phenylethylphenylacetate	3.767
Phenyl heptanol	3.478
Alpha-Santalol	3.800
Thibetolide (Trade name for 15-Hydroxypentadecanoic acid, lactone)	6.246
Delta-Undecalactone	3.830
Gamma-Undecalactone	4.140
Vetiveryl acetate	4.882
Ylangene	6.268

The higher ClogP materials are preferred, meaning that those materials with a ClogP value of 4.5 are preferred over those fragrance materials with a ClogP of 4; and those materials are preferred over the fragrance materials with a ClogP of 3.3.

The fragrance formulation of the present invention should have at least about 60 weight percent of materials with ClogP greater than 3.3, preferably greater than about 80 and more preferably greater than about 90 weight percent of materials with ClogP greater than 4.

Those with skill in the art appreciate that fragrance formulations are frequently complex mixtures of many fragrance ingredients. A perfumer commonly has several thousand fragrance chemicals to work from. Those with skill in the art appreciate that the present invention may contain a single ingredient, but it is much more likely that the present invention will comprise at least eight or more fragrance chemicals, more likely to

contain twelve or more and often twenty or more fragrance chemicals. The present invention also contemplates the use of complex fragrance formulations containing fifty or more fragrance chemicals, seventy five or more or even a hundred or more fragrance chemicals in a fragrance formulation.

Preferred fragrance materials will have both high ClogP and high vapor pressure. Among those having these properties are:

Para cymene, Caphene, Mandarinal Firm, Vivaldie, Terpinene, Verdox, Fenchyl acetate, Cyclohexyl isovalerate, Manzanate, Myrcene, Herbavert, Isobutyl isobutyrate, Tetrahydrocitral, Ocimene and Caryophyllene.

As described herein, the present invention is well suited for use in a variety of well-known consumer products such as laundry detergent and fabric softeners, liquid dish detergents, automatic dish detergents, as well as hair shampoos and conditioners. These products employ surfactant and emulsifying systems that are well known. For example, fabric softener systems are described in U. S. Patents 6,335,315, 5,674,832, 5,759,990, 5,877,145, 5,574,179; 5,562,849, 5,545,350, 5,545,340, 5,411,671, 5,403,499, 5,288,417, and 4,767,547, 4,424,134. Liquid dish detergents are described in U.S. Patents 6,069,122 and 5,990,065; automatic dish detergent products are described in U.S. Patents 6,020,294, 6,017,871, 5,968,881, 5,962,386, 5,939,373, 5,914,307, 5,902,781, 5,705,464, 5,703,034, 5,703,030, 5,679,630, 5,597,936, 5,581,005, 5,559,261, 4,515,705, 5,169,552, and 4,714,562. Liquid laundry detergents which can use the present invention include those systems described in U.S. Patents 5,929,022, 5,916,862, 5,731,278, 5,565,145, 5,470,507, 5,466,802, 5,460,752, 5,458,810, 5,458,809, 5,288,431, 5,194,639, 4,968,451, 4,597,898, 4,561,998, 4,550,862, 4,537,707, 4,537,706, 4,515,705, 4,446,042, and 4,318,818. Shampoo and conditioners that can employ the present invention include those described in U.S. Patents 6,162,423, 5,968,286, 5,935,561, 5,932,203, 5,837,661, 5,776,443, 5,756,436, 5,661,118, 5,618,523, 5,275,755, 5,085,857, 4,673,568, 4,387,090 and 4,705,681. All of the above mentioned U.S. Patents.

In addition to the fragrance materials that are to be encapsulated in the present invention, the present invention also contemplates the incorporation of solvent materials. The solvent materials are hydrophobic materials that are miscible in the fragrance materials used in the present invention. Suitable solvents are those having reasonable affinity for the fragrance chemicals and a ClogP greater than 3.3, preferably greater than 8 and most preferably greater than 10. Suitable materials include, but are not limited to triglyceride oil, mono and diglycerides, mineral oil, silicone oil, diethyl phthalate, polyalpha olefins, castor oil and isopropyl myristate. In a preferred embodiment the solvent materials are combined with fragrance materials that have high ClogP values as set forth above. It should be noted that selecting a solvent and fragrance with high affinity for each other will result in the most pronounced improvement in stability. Appropriate solvents may be selected from the following non-limiting list:

- Mono-, di- and tri-esters, and mixtures thereof, of fatty acids and glycerine. The fatty acid chain can range from C4-C26. Also, the fatty acid chain can have any level of unsaturation. For instance capric/caprylic triglyceride known as Neobee M5 (Stepan Corporation). Other suitable examples are the Capmul series by Abitec Corporation. For instance, Capmul MCM.
- Isopropyl myristate
- Fatty acid esters of polyglycerol oligomers:

$$R_2CO-[OCH_2-CH(OCOR_1)-CH_2O-]_n$$
 where R1 and R2 can be H or C4-26 aliphatic chains, or mixtures thereof, and n ranges between 2 – 50, preferably 2-30.
- Nonionic fatty alcohol alkoxylates like the Neodol surfactants by BASF, the Dobanol surfactants by Shell Corporation or the BioSoft surfactants by Stepan. The alkoxy group being ethoxy, propoxy, butoxy, or mixtures thereof. In addition, these surfactants can be end-capped with methyl groups in order to increase their hydrophobicity.
- Di- and tri-fatty acid chain containing nonionic, anionic and cationic surfactants, and mixtures thereof.

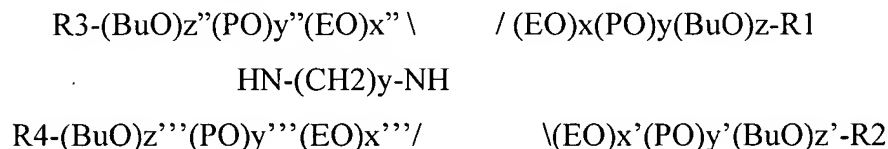
- Fatty acid esters of polyethylene glycol, polypropylene glycol, and polybutylene glycol, or mixtures thereof.
- Polyalphaolefins such as the ExxonMobil PureSym™ PAO line
- Esters such as the ExxonMobil PureSyn™ Esters
- Mineral oil
- Silicone oils such polydimethyl siloxane and polydimethylcyclsiloxane
- Diethyl phthalate
- Di-isodecyl adipate

The level of solvent in the core of the encapsulated fragrance material should be greater than about 30 weight percent, preferably greater than about 50 weight percent and most preferably greater than about 75 weight percent. In addition to the solvent it is preferred that higher ClogP fragrance materials are employed. It is preferred that greater than about 25 weight percent, preferably greater than 30 and more preferably greater than about 40 weight percent of the fragrance chemicals have ClogP values of greater than about 2.5, preferably greater than about 3 and most preferably greater than about 3.5. Those with skill in the art will appreciate that many formulations can be created employing various solvents and fragrance chemicals. The use of high ClogP fragrance chemicals will require a lower level of hydrophobic solvent than fragrance chemicals with lower ClogP to achieve similar stability. As those with skill in the art will appreciate, in a highly preferred embodiment high ClogP fragrance chemicals and hydrophobic solvents comprise greater than about 80, preferably more than about 90 and most preferably greater than 99 weight percent of the fragrance composition.

It has also been found that the addition of hydrophobic polymers to the core can also improve stability by slowing diffusion of the fragrance from the core. The level of polymer is normally less than 80% of the core by weight, preferably less than 50%, and most preferably less than 20%. The basic requirement for the polymer is that it be miscible or compatible with the other components of the core, namely the fragrance and other solvent. Preferably, the polymer also thickens or gels the core, thus further reducing diffusion. Polymers may be selected from the non-limiting group below:

- Copolymers of ethylene. Copolymers of ethylene and vinyl acetate (Elvax polymers by DOW Corporation). Copolymers of ethylene and vinyl alcohol (EVAL polymers by Kuraray). Ethylene/Acrylic elastomers such as Vamac polymers by Dupont).
- Poly vinyl polymers, such as poly vinyl acetate.
- Alkyl-substituted cellulose, such as ethyl cellulose (Ethocel made by DOW Corporation), hydroxypropyl celluloses (Klucel polymers by Hercules)
- Uncharged polyacrylates. Examples being (i) Amphomer, Demacryl LT and Dermacryl 79, made by National Starch and Chemical Company, (ii) the Amerhold polymers by Amerchol Corporation, and (iii) Acudyne 258 by ISP Corporation.
- Copolymers of acrylic or methacrylic acid and fatty esters of acrylic or methacrylic acid. These are side-chain crystallizing. Typical polymers of this type are those listed in U.S. Patents 4,830,855, 5,665,822, 5,783,302, 6,255,367 and 6,492,462. Examples of such polymers are the Intelimer Polymers, made by Landec Corporation.
- Polypropylene oxide.
- Polybutylene oxide of poly(tetra hydrofuran).
- Polyethylene terephthalate.
- Alkyl esters of poly(methyl vinyl ether) – maleic anhydride copolymers, such as the Gantrez copolymers and Omnirez 2000 by ISP Corporation.
- Carboxylic acid esters of polyamines. Examples of this are ester-terminated polyamide (ETPA) made by Arizona Chemical Company.
- Poly vinyl pyrrolidone (Luviskol series of BASF).
- Block copolymers of ethylene oxide, propylene oxide and/or butylenes oxide. These are known as the Pluronic and Synperonic polymers/dispersants by BASF.

- Another class of polymers include polyethylene oxide-co-propyleneoxide-co-butylene oxide polymers of any ethylene oxide/propylene oxide / butylene oxide ratio with cationic groups resulting in a net theoretical positive charge or equal to zero (amphoteric). The general structure is:



where R1, 2, 3, 4 is H or any alkyl of fatty alkyl chain group. Examples of such polymers are the commercially known as Tetronics by BASF Corporation.

We have also discovered that when capsules having cores containing a very large proportion of solvents with the appropriate ClogP values and/or with the high ClogP fragrance chemicals described above the encapsulated materials are actually capable of absorbing fragrance chemicals from surfactant-containing product bases. As is well appreciated by those with skill in the art, products such as, but not limited to fabric softeners, laundry detergents, bleaching products, shampoos and hair conditioners contain in their base formulas functional materials such as surfactants, emulsifying agents, detergent builders, whiteners, and the like along with fragrance chemicals. These products often aggressively absorb fragrance ingredients, most often due to the partially hydrophobic surfactant.

Most consumer products are made using an aqueous base, although some products use glycols, polyhydric alcohols, alcohols, or silicone oils as the dominant solvent or carrier. Absorption from these bases is also possible if the core is properly designed and used at the appropriate level in the base. Examples of these products include many deodorants and anti-perspirants.

In the product base the fragrance is used to provide the consumer with a pleasurable fragrance during and after using the product or to mask unpleasant odors from some of the functional ingredients used in the product. As stated above, one long standing problem with the use of fragrance in product bases is the loss of the fragrance

before the optimal time for fragrance delivery. We have discovered that with the proper selection of solvent and/or fragrance chemicals in the capsule core, the capsule will successfully compete for the fragrance chemicals present in the aqueous product base during storage. Eventually the core absorbs a significant quantity of fragrance, and finally an equilibrium level of fragrance is established in the core which is specific to the starting core composition and concentration in the base, type and concentration of the fragrance materials in the base, base composition, and conditions of storage. This ability to load the capsule core with fragrance material from the product base, particularly those product bases that contain a high concentration of surfactant proves that with judicious selection of core composition good fragrance stability within the core can be achieved.

Therefore, in another embodiment of the present invention is a method for providing encapsulated fragrance products through the re-equilibration of the fragrance materials from the product base into the capsules. The process includes providing a product base containing fragrance materials and capsules with a permeable shell, the capsules containing a solvent as defined above or with high ClogP fragrance materials. The solvents and high ClogP fragrance materials have an affinity for the fragrance material. In order to absorb fragrance materials that previously are not present in the core of the capsules, to re-equilibrate into the capsule core it is preferred that the capsules contain some void space or contain some lower ClogP fragrance materials that can partition out of the capsule into product base. Capsule shells with the appropriate degree of permeability are described in the application.

As described above capsules loaded with solvent and or high ClogP fragrance materials will absorb other fragrance materials from the product. In this embodiment of the invention, the capsule cores compete with the surfactant and primarily aqueous media of the products for fragrance materials placed in the product bases during storage. Eventually the cores absorb a significant quantity of fragrance, and finally an equilibrium level of fragrance is established in the core which is specific to a given starting core composition and concentration in the base, type and concentration of fragrance materials in the base, base compositions and conditions of storage. The self-loading of the cores in

bases that have high concentrations of surfactants also indicates that by judicious core selection fragrance stability within the core can be achieved.

As used herein stability of the products is measured at room temperature or above over a period of at least a week. More preferably the capsules of the present invention are allowed to be stored at room temperature for more than about two weeks and preferably more than about a month.

More specifically, the present invention provides a method of encapsulating a fragrance material comprising:

providing a product base containing non-encapsulated fragrance material and surfactant material;

providing a permeable capsule wherein the permeable capsule contains greater than about 70 weight percent fragrance material having a ClogP value of greater than about 3.3 or suitable hydrophobic solvent; and

allowing the non-encapsulated fragrance material and the permeable capsule material containing the fragrance material to come to equilibrium thereby transporting the non-encapsulated fragrance through the permeable shell wall into the interior of the capsule and retaining the fragrance contents of the permeable capsule.

In this embodiment of the invention a method for increasing the amount of a fragrance within a capsule comprising an aqueous base product that contains surfactant and fragrance, providing a capsule permeable to the fragrance when stored in the base, contained within said capsule greater than about 60 weight percent components selected from the group consisting of water insoluble solvent and fragrance chemicals having a ClogP value of greater than about 3.3; storing the aqueous product base and the porous capsule for at least about a week, thereby allowing the fragrance chemicals provided in the aqueous base to be transported through the capsule wall. As further described, the selection of solvents and fragrance chemicals with correct ClogP values results in

capsules with higher fragrance loading. The higher fragrance loading results in higher fragrance delivery than what was previously possible with fragrance provided in the aqueous base or provided in an oil included in the base. For example, when the capsules are employed in a fabric conditioner product it was discovered that the capsules of the present invention deposited fragrance as measured by the breaking of the capsules and the measurement of fragrance in the headspace to be more than 100% greater than fragrance alone or fragrance and solvent combinations deposited on the same cloth. In some instances the headspace measurement indicated an increase of more than 200 and even greater than about 300 percent when measuring fragrance in the headspace when employing the capsules with high ClogP materials and/or suitable solvents when compared to fragrance or fragrance solvent combinations.

In another embodiment of the present invention a sacrificial solvent is initially placed with the capsule. A sacrificial solvent is a solvent having a low ClogP value of from about 1 to about 3, preferably from about 1.25 to about 2.5, and most preferably from about 1.5 to about 2. If the ClogP of the sacrificial solvent is too low, the sacrificial solvents will be lost in the manufacture of the capsule materials. Suitable sacrificial solvents include benzyl acetate, and octanol.

The present invention provides a method of making capsules containing high Clog P liquid fragrance materials within the capsule comprising the steps of:

providing a sacrificial solvent having a ClogP value of from about 1 to about 3;

encapsulating the sacrificial solvent with a permeable encapsulate material;

providing the encapsulated sacrificial solvent in a liquid environment containing fragrance materials with ClogP of greater than about 3.3;

allowing the capsules containing the sacrificial solvent to come to equilibrium with the environment containing the high Clog P fragrance materials;

whereby at least 20 weight percent of the sacrificial solvent migrates from the capsule into the environment.

Preferably more than 30 and more than 40 weight percent of the sacrificial solvent will migrate from the capsules to the environment, thereby allowing the capsules to increase the level of high ClogP fragrance material inside the capsule by more than 10 weight percent, preferably more than 20 and most preferably more than 30 weight percent over the original weight of ClogP materials above 3.3 originally found inside the capsule.

The time for this migration of the sacrificial solvent from the interior of the permeable capsule to the environment, thereby creating space within the capsule for the high ClogP materials to migrate into the capsule is as short as seven to ten days. This means that under normal product manufacture, shipping and distribution, the sacrificial solvent will have sufficient time to migrate from the capsule interior, thereby creating free volume and allowing the preferred higher ClogP materials to migrate into the interior. Of course, longer periods of time will allow greater amounts of the sacrificial solvent to exit through the capsule wall and create more free volume and eventually a true equilibrium will occur where at a given temperature, the migration of sacrificial solvent out of the capsule and migration of high ClogP material into the capsule will eventually end.

An important advantage of the migration technology is that capsules containing sacrificial solvent can be prepared in large quantities, and placed in various fragrance environments. This means that through the proper selection of fragrance materials, capsules and sacrificial solvent, an encapsulated fragrance materials can be prepared without having to encapsulate each specific custom fragrance.

The invention in its various embodiments provides a capsule core composition that is able to retain a significant amount of fragrance within the capsule core and to deliver the higher level of fragrance contained therein at the desired time. We have

discovered that the capsule products of the present invention under specified times of time, temperature, and concentration in various product bases retain more than about 10 weight percent, preferably more than 30 and most preferably more than 70 weight percent of the fragrance materials originally encapsulated.

Fragrance retention within the capsule may be measured directly after storage at a desired temperature and time periods such as six weeks, two months, three months or more. The preferred manner is to measure total headspace of the product at the specified time and to compare the results to the headspace of a control product made to represent 0% retention via direct addition of the total amount of fragrance present. Alternatively, the product base may be performance tested after the storage period and the performance compared to the fresh product, either analytically or by sensory evaluation. This more indirect measurement often involves either measuring the fragrance headspace over a substrate used with the product, or odor evaluation of the same substrate.

Encapsulation of fragrances is known in the art, see for example U.S. Patent Nos. 2,800,457, 3,870,542, 3,516,941, 3,415,758, 3,041,288, 5,112,688, 6,329,057, and 6,261,483. Another discussion of fragrance encapsulation is found in the Kirk-Othmer Encyclopedia. A preferred disclosure of fragrance encapsulation is found in U.S. Serial Numbers 10/460,610 and 10/464,434 both filed June 12, 2003.

Once the fragrance material is encapsulated a cationically charged water-soluble polymer can be applied to the fragrance encapsulated polymer. This water-soluble polymer can also be an amphoteric polymer with a ratio of cationic and anionic functionalities resulting in a net total charge of zero and positive, i.e., cationic. Those skilled in the art would appreciate that the charge of these polymers can be adjusted by changing the pH, depending on the product in which this technology is to be used. Any suitable method for coating the cationically charged materials onto the encapsulated fragrance materials can be used. The nature of suitable cationically charged polymers for assisted capsule delivery to interfaces depends on the compatibility with the capsule wall chemistry since there has to be some association to the capsule wall. This association can

be through physical interactions, such as hydrogen bonding, ionic interactions, hydrophobic interactions, electron transfer interactions or, alternatively, the polymer coating could be chemically (covalently) grafted to the capsule or particle surface. Chemical modification of the capsule or particle surface is another way to optimize anchoring of the polymer coating to capsule or particle surface. Furthermore, the capsule and the polymer need to want to go to the desired interface and, therefore, need to be compatible with the chemistry (polarity, for instance) of that interface. Therefore, depending on which capsule chemistry and interface (e.g., cotton, polyester, hair, skin, wool) is used the cationic polymer can be selected from one or more polymers with an overall zero (amphoteric: mixture of cationic and anionic functional groups) or net positive charge, based on the following polymer backbones: polysaccharides, polypeptides, polycarbonates, polyesters, polyolefinic (vinyl, acrylic, acrylamide, poly diene), polyester, polyether, polyurethane, polyoxazoline, polyamine, silicone, polyphosphazine, olyaromatic, poly heterocyclic, or polyionene, with molecular weight (MW) ranging from about 1,000 to about 1000,000,000, preferably from about 5,000 to about 10,000,000. As used herein molecular weight is provided as weight average molecular weight. Optionally, these cationic polymers can be used in combination with nonionic and anionic polymers and surfactants, possibly through coacervate formation.

A more detailed list of cationic polymers that can be used to coat the encapsulated fragrance is provided below:

Polysaccharides include but are not limited to guar, alginates, starch, xanthan, chitosan, cellulose, dextrans, arabic gum, carrageenan, hyaluronates. These polysaccharides can be employed with:

- (a) cationic modification and alkoxy-cationic modifications, such as cationic hydroxyethyl, cationic hydroxy propyl. For example, cationic reagents of choice are 3-chloro-2-hydroxypropyl trimethylammonium chloride or its epoxy version. Another example is graft-copolymers of polyDADMAC on cellulose like in Celquat L-200 (Polyquaternium-4), Polyquaternium-10 and Polyquaternium-24, commercially available from National Starch, Bridgewater, N.J.;
- (b) aldehyde, carboxyl, succinate, acetate, alkyl, amide, sulfonate, ethoxy, propoxy, butoxy, and combinations of these functionalities. Any combination of Amylose and Amylopectin and overall molecular weight of the polysaccharide; and
- (c) any hydrophobic modification (compared to the polarity of the polysaccharide backbone).

The above modifications described in (a), (b) and (c) can be in any ratio and the degree of functionalization up to complete substitution of all functionalizable groups, and as long as the theoretical net charge of the polymer is zero (mixture of cationic and anionic functional groups) or preferably positive. Furthermore, up to 5 different types of functional groups may be attached to the polysaccharides. Also, polymer graft chains may be differently modified than the backbone. The counter ions can be any halide ion or organic counter ion. U.S. Patent Nos. 6,297,203 and U.S. 6,200,554.

Another source of cationic polymers contain protonatable amine groups so that the overall net charge is zero (amphoteric: mixture of cationic and anionic functional groups) or positive. The pH during use will determine the overall net charge of the

polymer. Examples are silk protein, zein, gelatin, keratin, collagen and any polypeptide, such as polylysine.

Further cationic polymers include poly vinyl polymers, with up to 5 different types of monomers, having the monomer generic formula $-C(R_2)(R_1)-CR_2R_3-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). Where R_1 is any alkanes from C1-C25 or H; the number of double bonds ranges from 0-5. Furthermore, R_1 can be an alkoxyated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and C1-C25 alkyl chain length. R_1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. In the above formula R_2 is H or CH_3 ; and R_3 is $-Cl$, $-NH_2$ (i.e. poly vinyl amine and its copolymers with N-vinyl formamide, known as Lupamin 9095 from BASF Corporation), $-NHR_1$, $-NR_1R_2$, $-NR_1R_2R_6$ (where $R_6 = R_1, R_2$, or $-CH_2-COOH$ or its salt), $-NH-C(O)-H$, $-C(O)-NH_2$ (amide), $-C(O)-N(R_2)(R_2')(R_2'')$, $-OH$, styrene sulfonate, pyridine, pyridine-N-oxide, quaternized pyridine, imidazolinium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, alkyl-substituted pyrrolidone, caprolactam or pyridine, phenyl- R_4 or naphthalene- R_5 where R_4 and R_5 are R_1, R_2, R_3 , sulfonic acid or its alkali salt $-COOH$, $-COO-$ alkali salt, ethoxy sulphate or any other organic counter ion. Any mixture of these R_3 groups may be used. Further suitable cationic polymers containing hydroxy alkyl vinyl amine units, as disclosed in U.S. Patent No 6,057,404.

Another class of materials are polyacrylates, with up to 5 different types of monomers, having the monomer generic formula:

$-CH(R_1)-C(R_2)(CO-R_3-R_4)-$. Any co-monomer from the types listed in this specification may also be used. The overall polymer will have a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). In the above formula R_1 is any alkane from C1-C25 or H with number of double bonds from 0-5, aromatic moieties, polysiloxane, or mixtures thereof. Furthermore, R_1 can be an alkoxyated fatty alcohol with any alkoxy carbon-length, number of alkoxy groups and

C1-C25 alkyl chain length. R1 can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R2 is H or CH₃; R3 is alkyl alcohol C1-25 or an alkylene oxide with any number of double bonds, or R3 may be absent such that the C=O bond is (via the C-atom) directly connected to R4. R4 can be: -NH₂, NHR₁, -NR₁R₂, -NR₁R₂ R₆ (where R₆ = R₁, R₂, or -CH₂-COOH or its salt), -NH-C(O)-, sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group, H, OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolinium halide, imidazolium halide, imidazol, piperidine, -OR₁, -OH, -COOH alkali salt, sulfonate, ethoxy sulphate, pyrrolidone, caprolactam, phenyl-R₄ or naphthalene-R₅ where R₄ and R₅ are R₁, R₂, R₃, sulfonic acid or its alkali salt or organic counter ion. Any mixture or these R₃ groups may be used. Also, glyoxylated cationic polyacrylamides can be used. Typical polymers of choice are those containing the cationic monomer dimethylaminoethyl methacrylate (DMAEMA) or methacrylamidopropyl trimethyl ammonium chloride (MAPTAC). DMAEMA can be found in Gafquat and Gaffix VC-713 polymers from ISP. MAPTAC can be found in BASF's Luviquat PQ11 PN and ISP's Gafquat HS100.

Another group of polymers that can be used are those that contain cationic groups in the main chain or backbone. Included in this group are:

- (1) polyalkylene imines such as polyethylene imine, commercially available as Lupasol from BASF. Any molecular weight and any degree of crosslinking of this polymer can be used in the present invention;
- (2) ionenes having the general formula set forth as

$$-[N(+)R_1R_2-A_1-N(R_5)-X-N(R_6)-A_2-N(+)R_3R_4-A_3]_n-2Z-$$
as disclosed in U.S. Patent Nos. 4,395,541 and U.S. 4,597,962;
- (3) adipic acid/dimethyl amino hydroxypropyl diethylene triamine copolymers, such as Cartaretin F-4 and F-23, commercially available from Sandoz;

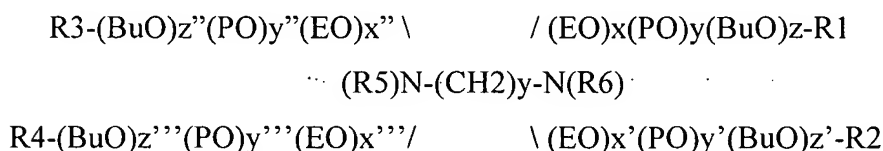
- (4) polymers of the general formula-[N(CH₃)₂-(CH₂)_x-NH-(CO)-NH-(CH₂)_y-N(CH₃)₂)-(CH₂)_z-O-(CH₂)_p]_n-, with x, y, z, p=1-12, and n according to the molecular weight requirements. Examples are Polyquaternium 2 (Mirapol A-15), Polyquaternium-17 (Mirapol AD-1), and Polyquaternium-18 (Mirapol AZ-1).

Other polymers include cationic polysiloxanes and cationic polysiloxanes with carbon-based grafts with a net theoretical positive charge or equal to zero (mixture of cationic and anionic functional groups). This includes cationic end-group functionalized silicones (i.e. Polyquaternium-80). Silicones with general structure: -[Si(R₁)(R₂)-O-]_x-[Si(R₃)(R₂)-O-]_y- where R₁ is any alkane from C₁-C₂₅ or H with number of double bonds from 0-5, aromatic moieties, polysiloxane grafts, or mixtures thereof. R₁ can also be a liquid crystalline moiety that can render the polymer thermotropic liquid crystalline properties, or the alkanes selected can result in side-chain melting. R₂ can be H or CH₃ and R₃ can be -R₁-R₄, where R₄ can be -NH₂, -NHR₁, -NR₁R₂, -NR₁R₂R₆ (where R₆ = R₁, R₂, or -CH₂-COOH or its salt), -NH-C(O)-, -COOH, -COO- alkali salt, any C₁-25 alcohol, -C(O)-NH₂ (amide), -C(O)-N(R₂)(R_{2'})(R_{2''}), sulfo betaine, betaine, polyethylene oxide, poly(ethyleneoxide/propylene oxide/butylene oxide) grafts with any end group, H, -OH, styrene sulfonate, pyridine, quaternized pyridine, alkyl-substituted pyrrolidone or pyridine, pyridine-N-oxide, imidazolinium halide, imidazolium halide, imidazol, piperidine, pyrrolidone, caprolactam, -COOH, -COO- alkali salt, sulfonate, ethoxy sulphate phenyl-R₅ or naphthalene-R₆ where R₅ and R₆ are R₁, R₂, R₃, sulfonic acid or its alkali salt or organic counter ion. R₃ can also be -(CH₂)_x-O-CH₂-CH(OH)-CH₂-N(CH₃)₂-CH₂-COOH and its salts. Any mixture of these R₃ groups can be selected. X and y can be varied as long as the theoretical net charge of the polymer is zero (amphoteric) or positive. In addition, polysiloxanes containing up to 5 different types of monomeric units may be used. Examples of suitable polysiloxanes are found in U.S. Patent Nos. 4,395,541 4,597,962 and U.S.6,200,554. Another group of polymers that can be used to improve capsule/particle deposition are phospholipids that are modified with cationic polysiloxanes. Examples of these polymers are found in U.S.

Patent No. 5,849,313; PCT Patent Application 9518096A1 and European Patent EP0737183B1.

Furthermore, copolymers of silicones and polysaccharides and proteins can be used (Crodasone Series).

Another class of polymers include polyethylene oxide-co-propyleneoxide-co-butylene oxide polymers of any ethylene oxide/propylene oxide / butylene oxide ratio with cationic groups resulting in a net theoretical positive charge or equal to zero (amphoteric). The general structure is:



where R1, 2, 3, 4 is -NH2, -N(R)3- X+, R with R being H or any alkyl group. R5, 6 is -CH3 or H. Counter ions can be any halide ion or organic counter ion. X, Y, may be any integer, any distribution with an average and a standard deviation and all 12 can be different. Examples of such polymers are the commercially available TETRONIC brand polymers.

Suitable polyheterocyclic (the different molecules appearing in the backbone) polymers include the piperazine-alkylene main chain copolymers disclosed in Ind. Eng. Chem. Fundam., (1986), 25, pp.120-125, by Isamu Kashiki and Akira Suzuki.

Also suitable for use in the present invention are copolymers containing monomers with cationic charge in the primary polymer chain. Up to 5 different types of monomers may be used. Any co-monomer from the types listed in this specification may also be used. Examples of such polymers are poly diallyl dimethyl ammonium halides (PolyDADMAC) copolymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolinium halides, etc. These polymers are disclosed in Henkel

EP0327927A2 and PCT Patent Application 01/62376A1. Also suitable are Polyquaternium-6 (Merquat 100), Polyquaternium-7 (Merquats S, 550, and 2200), Polyquaternium-22 (Merquats 280 and 295) and Polyquaternium-39 (Merquat Plus 3330), available from Onda Nalco.

Polymers containing non-nitrogen cationic monomers of the general type $\text{-CH}_2\text{-C(R}_1\text{)(R}_2\text{-R}_3\text{-R}_4\text{)-}$ can be used with:

R1 being a -H or C1-C20 hydrocarbon. R2 is a disubstituted benzene ring or an ester, ether, or amide linkage. R3 is a C1-C20 hydrocarbon, preferably C1-C10, more preferably C1-C4. R4 can be a trialkyl phosphonium, dialkyl sulfonium, or a benzopyrilium group, each with a halide counter ion. Alkyl groups for R4 are C1-C20 hydrocarbon, most preferably methyl and t-butyl. These monomers can be copolymerized with up to 5 different types of monomers. Any co-monomer from the types listed in this specification may also be used.

Substantivity of these polymers may be further improved through formulation with cationic, amphoteric and nonionic surfactants and emulsifiers, or by coacervate formation between surfactants and polymers or between different polymers. Combinations of polymeric systems (including those mentioned previously) may be used for this purpose as well as those disclosed in EP1995/000400185.

Furthermore, polymerization of the monomers listed above into a block, graft or star (with various arms) polymers can often increase the substantivity toward various surfaces. The monomers in the various blocks, graft and arms can be selected from the various polymer classes listed in this specification.

Polymers that are known as deposition aids, and in a preferred embodiment are also cationic can be found in the following resources:

Encyclopedia of Polymers and Thickeners for Cosmetics, Robert Lochhead and William From, in Cosmetics & Toiletries, Vol. 108, May 1993, pp. 95-138;

Modified Starches: Properties & Uses, O. B. Wurzburg, CRC Press, 1986.
Specifically, Chapters 3, 8, and 10;

U.S. Patent Nos. 6,190,678 and 6,200,554; and

PCT Patent Application WO 01/62376A1 assigned to Henkel.

The preferred cationically charged materials are selected from the group consisting of cationically modified starch and cationically modified guar, polymers comprising poly diallyl dimethyl ammonium halides (PolyDADMAC), and copolymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolinium halides, and the like. For instance, Polyquaternium-6, 7, 22 and 39, all available from Ondo Nalco.

The preferred cationic starch has a molecular weight of from about 100,000 to about 500,000, preferably from about 200,000 to about 10,000,000 and most preferably from about 250,000 to about 5,000,000. The preferred cationic starch products are HI-CAT CWS42 and HI-CAT 02 and are commercially available from ROQUETTE AMERICA, Inc.

The preferred cationic guar has a molecular weight of from about 50,000 to about 5,000,000. The preferred cationic guar products are Jaguar C-162 and Jaguar C-17 and are commercially available from Rhodia Inc.

The level of cationic polymer is from about 1% to about 3000%, preferably from about 5% to about 1000% and most preferably from about 10% to about 500% of the fragrance containing compositions, based on a ratio with the fragrance on a dry basis.

The weight ratio of the encapsulating polymer to fragrance is from about 1:25 to about 1:1. Preferred products have had the weight ratio of the encapsulating polymer to fragrance varying from about 1:10 to about 4:96.

For example, if a capsule blend has 20 weight % fragrance and 20 weight % polymer, the polymer ratio would be (20/20) multiplied by 100 (%) = 100%.

Preferred encapsulating polymers include those formed from melamine-formaldehyde or urea-formaldehyde condensates, as well as similar types of aminoplasts. Additionally, capsules made via the simple or complex coacervation of gelatin are also preferred for use with the coating. Capsules having shell walls comprised of polyurethane, polyamide, polyolefin, polysaccharide, protein, silicone, lipid, modified cellulose, gums, polyacrylate, polyphosphate, polystyrene, and polyesters or combinations of these materials are also functional.

A representative process used for aminoplast encapsulation is disclosed in U.S. Patent No. 3,516,941 though it is recognized that many variations with regard to materials and process steps are possible. A representative process used for gelatin encapsulation is disclosed in U.S. Patent No. 2,800,457 though it is recognized that many variations with regard to materials and process steps are possible. Both of these processes are discussed in the context of fragrance encapsulation for use in consumer products in U.S. Patent Nos. 4,145,184 and 5,112,688, respectively.

Particle and capsule diameter can vary from about 10 nanometers to about 1000 microns, preferably from about 50 nanometers to about 100 microns and is most preferably from about 2 to about 15 microns. The capsule distribution can be narrow, broad, or multi-modal. Multi-modal distributions may be composed of different types of capsule chemistries.

Well known materials such as solvents, surfactants, emulsifiers, and the like can be used in addition to the polymers described above to encapsulate the fragrance without departing from the scope of the present invention. It is understood that the term encapsulated is meant to mean that the fragrance material is substantially covered in its entirety. Encapsulation can provide pore vacancies or interstitial openings depending on

the encapsulation techniques employed. More preferably the entire fragrance material portion of the present invention is encapsulated.

The present invention, the encapsulated fragrance is well suited for wash-off products. Wash-off products are understood to be those products that are applied for a given period of time and then are removed. These products are common in areas such as laundry products, and include detergents, fabric conditioners, and the like; as well as personal care products which include shampoos, hair rinses, body washes, soaps and the like.

As described herein, the present invention is well suited for use in a variety of well-known consumer products such as laundry detergent and fabric softeners, liquid dish detergents, automatic dish detergents, as well as hair shampoos and conditioners. These products employ surfactant and emulsifying systems that are well known. For example, fabric softener systems are described in U.S. Patents 6,335,315, 5,674,832, 5,759,990, 5,877,145, 5,574,179; 5,562,849, 5,545,350, 5,545,340, 5,411,671, 5,403,499, 5,288,417, 4,767,547, 4,424,134. Liquid dish detergents are described in 6,069,122 and 5,990,065; automatic dish detergent products are described in 6,020,294, 6,017,871, 5,968,881, 5,962,386, 5,939,373, 5,914,307, 5,902,781, 5,705,464, 5,703,034, 5,703,030, 5,679,630, 5,597,936, 5,581,005, 5,559,261, 4,515,705, 5,169,552, and 4,714,562. Liquid laundry detergents which can use the present invention include those systems described in 5,929,022, 5,916,862, 5,731,278, 5,565,145, 5,470,507, 5,466,802, 5,460,752, 5,458,810, 5,458,809, 5,288,431, 5,194,639, 4,968,451, 4,597,898, 4,561,998, 4,550,862, 4,537,707, 4,537,706, 4,515,705, 4,446,042, and 4,318,818. Shampoo and conditioners that can employ the present invention include 6,162,423, 5,968,286, 5,935,561, 5,932,203, 5,837,661, 5,776,443, 5,756,436, 5,661,118, 5,618,523, 5,275,755, 5,085,857, 4,673,568, 4,387,090 and 4,705,681. All of the above mentioned U.S. Patents are incorporated by reference as if set forth in their entirety.

We have discovered that the present invention is advantageously applied to products, including fabric rinse conditioners, having a pH of less than 7, preferably less than about 5 and most preferably less than about 4.

A better product, including wash-off products such as fabric rinse conditioner is also obtained when the salt level is limited. The improvement in the fabric rinse conditioner is noted by a longer lasting and/or improved delivery of fragrance. One method of improving the delivery of the encapsulated fragrance is to limit the amount of salt in the product base. Preferably the level of salt in the rinse conditioner product is less than or equal to about 1 weight percent by weight in the product, preferably less than about 0.5 weight percent and most preferably less than about 0.1 weight percent.

More specifically we have discovered that limiting the level of calcium chloride will improve the delivery of the fragrance using the encapsulated fragrance of the present invention. Improved fragrance delivery is provided by limiting the amount of calcium chloride to less than about 2 weight percent, typically less than 1 weight percent and more preferably less than 0.5 weight percent. As it is known in the art, calcium chloride is added to control viscosity of the formulations, so there is trade-off between the viscosity and fragrance delivery. We have discovered that limiting the level of calcium chloride level as set forth above is particularly advantageous in fabric rinse conditioner products.

Another means for improving the performance of delivery of the encapsulated fragrance of the present invention is to limit the level of some softening agents. We have discovered that limiting the softening actives, such as triethanolamine quaternary, diethanolamine quaternary, ACCOSOFT cationic surfactants (Stepan Chemical), or ditallow dimethyl ammonium chloride (DTDMAC), to an amount of from about 5 to about 40 weight percent of the product, preferably from about 5 to about 30 and more preferably from about 5 to 15 weight percent of a fabric rinse conditioner product will improve the performance of the fragrance. The above softening agents are well known in the art and are disclosed in U.S. Patents 6,521,589 and 6,180,594.

Yet another means for improving fragrance delivery of the present invention is to limit the level of the non-ionic surfactants employed in the product, including a fabric softening product. Many non-ionic surfactants are known in the art and include alkyl ethoxylate, commercially available as NEODOL (Shell Oil Company), nonyl phenol ethoxylate, TWEEN surfactants (ICI Americas Inc.), and the like. We have discovered that the encapsulated fragrance of the present invention are advantageously used when the non-ionic surfactant level is below about 5 weight percent of the product, preferably less than about 1 weight percent and most preferably less than 0.5 weight percent.

Yet another means for enhancing the fabric softener product is to limit the level of co-solvent included in the fabric softener in addition to water. Reducing the level of co-solvents such as ethanol and isopropanol to less than about 5 weight percent of the product, preferably less than about 2 and most preferably less than about 1 weight percent of the fabric softener product has been found to improve fragrance delivery.

Improved fragrance performance includes longer lasting fragrance, improved substantivity of the fragrance on cloth or the ability to provide improved fragrance notes, such as specific fragrance notes through the use of the present invention.

While the above description is primarily to fabric rinse conditioner products, additional studies for shampoos, detergent and other cleaning products have also led to preferred embodiments for these products as well.

As was found for fabric rinse conditioners, additional studies have determined that lower pH is desirable for the delivery of fragrance when used in the product base. The preferred bases are neutral or mildly acidic, preferably having a pH of 7, more preferably less than about 5 and most preferably less than about 4 for shampoos, detergent and other cleaning products.

We have found that powder detergent and other cleaning products provide enhanced fragrance delivery when the material coating the encapsulating polymer is also neutral or slightly acidic. Preferred materials are NaHSO_4 , acetic acid, citric acid and other similar acidic materials and their mixtures. These materials have a pH of less than about 7, preferably less than about 5 and most preferably less than about 4.

As was described with fabric rinse conditioners, lower surfactant levels were advantageously employed in shampoos, detergents and other cleaning products bases with the present invention. The level of surfactant is preferably less than about 30, more preferably less than about 20 and most preferably less than about 10 weight percent of the product base. A similar finding was found with preferred levels of salt in shampoos, detergents and other cleaning products as was found in fabric rinse conditioners. The salt level is preferably less than about 5 weight percent, more preferably less than about 2 and most preferably less than 0.5 weight percent of the product.

Lower solvent levels found in the base improves the fragrance delivery in shampoos, detergents and other cleaning products as well. Solvents, include but are not limited to, ethanol, isopropanol, dipropylene glycol in addition to the water base and the hydrotope level is preferably less than 5 weight percent, preferably less than about 2 and most preferably less than 1 weight percent of the total product base.

A preferred surfactant base for shampoos, detergents and other cleaning products was found to be ethoxylated surfactants such as alkyl ethoxylated sulfates, $(\text{C}_{12}\text{-C}_{14})$ (ethylene oxide) $n\text{SO}_4\text{M}$; or ethoxylated carboxylate surfactants $(\text{C}_{12}\text{-C}_{14})$ (Ethylene oxide) $n\text{COOM}$ where n is from 1 to about 50 and M is Na^+ , K^+ or NH_4^+ cation. Other preferred anionic surfactants are alkoyl isthionates such as sodium cocoly isthionate, taurides, alpha olefin sulphonates (i.e. Bioterge, Stepan Corporation), sulfosuccinates such as Standapol SH-100 (Cognis) and disodium laureth sulfosuccinate (Stepan Mild SL3-BA, Stepan Corporation). A more preferred class of surfactants for use in the present invention was zwitterionic surfactants such as the alkyl amine oxides, amidealkyl hydroxysultaines like amidopropyl hydroxyl sultaine (Amphosol CS-50, Stepan

Corporation), amphotacetates such as sodium cocamphoacetate (Amphosol IC, Stepan Corporation), betaines and sulfobetaines. Zwitterionic surfactants are disclosed in greater detail in U.S. Patent 6,569,826. Other commercially available surfactants are AMPHOSOL series of betaines (Stepan Chemical); TEGOTIAN by Goldschmidt; and HOSTAPAN and ARKOPAN by Clariant.

The most preferred surfactant system to be employed with the encapsulated fragrance system of the present invention was found to be non-ionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 50 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Other ethoxylated nonionic surfactants that are suitable are polyethylene glycol (MW=200-6000) esters of fatty acids, ethylene oxide-propylene oxide-butylene oxide block copolymers such as the Pluronic and Tetronic polymers made by BASF, and ethoxylated alkanolamides such as PEG-6 cocamide (Ninol C-5, Stepan Corporation). Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, polyhydroxyamides (glucamide), polyglycerol fatty acid esters, alkyl pyrrolidone-based surfactants (Surfadone LP-100 and LP300, ISP Corporation), dialkyl phthalic acid amides (distearyl phthalic acid amide or Stepan SAB-2 by Stepan Corporation), alkyl alkanolamides such as Laureth Diethanolamide (Ninol 30-LL, Stepan Corporation). These nonionic surfactants are disclosed in U.S. Patent 6,517,588.

In addition, Gemini surfactants can be used, such as the Gemini polyhydroxy fatty acid amides disclosed in U.S. Patent 5,534,197. Furthermore, structured liquids can be used that contain lamellar vesicles or lamellar droplets, as disclosed in WO 9712022 A1, WO 9712027 A1, 5,160,655, and 5,776,883.

The rinse-off products that are advantageously used with the polymer encapsulated fragrance of the present invention include laundry detergents, fabric

softeners, bleaches, brighteners, personal care products such as shampoos, rinses, creams, body washes and the like. These may be liquids, solids, pastes, or gels, of any physical form. Also included in the use of the encapsulated fragrance are applications where a second active ingredient is included to provide additional benefits for an application. The additional beneficial ingredients include fabric softening ingredients, skin moisturizers, sunscreen, insect repellent and other ingredients as may be helpful in a given application. Also included are the beneficial agents alone, that is without the fragrance.

While the preferred coating materials may be simply dissolved in water and mixed with a suspension of capsules prior to addition to the final product, other modes of coating use and application are also possible. These modes include drying the coating solution in combination with the capsule suspension for use in dry products such as powder detergents, or using higher concentrations of coating such that a gel structure is formed, or combining the coating material with other polymers or adjuvants which serve to improve physical characteristics or base compatibility. Drying or reducing the water content of the capsule suspension prior to coating addition is also possible, and may be preferable when using some coating materials. Further, when using some coating materials it is possible to add the coating to the application base separately from the encapsulated fragrance.

Solvents or co-solvents other than water may also be employed with the coating materials. Solvents that can be employed here are (i) polyols, such as ethylene glycol, propylene glycol, glycerol, and the like, (ii) highly polar organic solvents such as pyrrolidine, acetamide, ethylene diamine, piperazine, and the like, (iii) humectants/plasticizers for polar polymers such as monosaccharides (glucose, sucrose, etc.), amino acids, ureas and hydroxyethyl modified ureas, and the like, (iv) plasticizers for less polar polymers, such as diisodecyl adipate (DIDA), phthalate esters, and the like.

The coating polymer(s) may also be added to a suspension of capsules that contain reactive components such that the coating becomes chemically (covalently) grafted to the capsule wall, or the coating polymer(s) may be added during the

crosslinking stage of the capsule wall such that covalent partial grafting of the coating takes place.

The present invention also includes the incorporation of a silicone or a siloxane material into a product that contains encapsulated fragrances of the present invention. As used herein silicone is meant to include both silicone and siloxane materials. Also included in the definition of silicone materials are the cationic and quaternized of the silicones. These materials are well known in the art and include both linear and branched polymers.

In addition to silicones, the present invention also includes the use of mineral oils, triglyceride oils and sucrose polyester materials in a similar matter as the silicone materials. For brevity, these materials are understood to be included in the term silicone as used in this specification unless noted to the contrary. Those with skill in the art will also appreciate that it is possible to incorporate a silicone in combination with mineral oils and the like in carrying out the present invention.

The silicone material is preferably admixed to the encapsulated fragrance-containing product after the fragrance materials are encapsulated. Optionally, the silicone material may be mixed directly with the product base either before or after the encapsulated fragrance has been added.

Suitable silicone materials include amodimethicone, polymethylalkyl siloxanes, polydimethylalkyl siloxanes, dimethicone, dimethicone copolyol, dimethiconol, disiloxane, cyclohexasiloxane, cyclomethicone, cyclopentasiloxane, phenyl dimethicone, phenyl trimethicone, silicone quaternary materials including silicone quaternium-8, and silicone quaternium-12, trimethylsiloxyamidodimethicone, trimethylsiloxy silicate and the like. These materials are commercially well known materials and are available from suppliers such as Dow Corning, Shin-Etsu, Wacker Silicones Corporation and the like. The preferred silicon is Dow Corning 245 Fluid (Dow Corning, Midland Michigan), which is described as containing greater than about 60 weight percent

decamethylcyclopentasiloxane and less than or equal to about 4 weight percent dimethylcyclodisiloxanes.

Amino functional silicone oils such as those described in U.S. Patents 6,355,234 and 6,436,383.

Capsules made via various methods, including melamine-formaldehyde polymerization, urea-formaldehyde polymerization, melamine-formaldehyde cross-linking of suitable polymers, and urea-formaldehyde cross-linking of suitable polymers are permeable to fragrance molecules when placed in aqueous surfactant dispersions typical of consumer product bases. Fragrance molecules thus leach from the core of the capsule to the external base, resulting in a decline of performance over time.

Those with skill in the art will appreciate that the diffusion of the fragrance material will depend on various factors including the selection of the fragrance materials, the encapsulating polymer, the surfactant level found in the product, and the physical parameters of the encapsulated particles. By physical properties it is meant such factors such as the thickness of the core, the thickness of the shell, and the relative diameter of the particles. Referring to Figure 1, the shell wall of the particle 10 is depicted and the core 20 containing the fragrance and solvent stabilizer is depicted. Optional secondary coatings on the shell wall are not depicted for clarity.

In order to demonstrate the invention, the following examples were conducted. All U.S. Patent and Patent applications referenced herein, are hereby incorporated by reference as if set forth in their entirety. The following disclosures are provided to exemplify the present invention

Unless noted to the contrary all weights are weight percent and all fragrance chemicals used herein are available from International Flavors & Fragrances Inc., New York, NY. Upon review of the foregoing, numerous adaptations, modifications and alterations will occur to the reviewer. These adaptations, modifications, and alterations

will all be within the spirit of the invention. Accordingly, reference should be made to the appended claims in order to ascertain the scope of the present invention.

EXAMPLE 1

Cationic polymer-coated capsules were prepared by mixing uncoated fragrance-containing capsules with the cationic polymeric deposition aid at the desired level. This mixing can be done during the manufacturing process of the capsules or by post-addition of the cationic deposition aid as a solution. The uncoated capsules were prepared by interfacial polymerization of fragrance droplets. To make the capsule slurry, a copolymer of acrylamide and acrylic acid was first dispersed in water together with a methylated melamine-formaldehyde resin. These two components were allowed to react under acidic conditions. Fragrance was then added into the solution and droplets of the desired size were achieved by high shear homogenization. Curing of the polymeric layer around the fragrance droplets was achieved by increasing the temperature to 50-85°C.

EXAMPLE 2

A slurry of capsules having shell walls composed of an acrylamide-acrylic acid co-polymer cross-linked with melamine-formaldehyde resin as described in Example 1 was mixed with a concentrated fabric conditioner. The fabric conditioner was commercially obtained and did not contain fragrance. The capsule slurry contained approximately 25 weight % fragrance, and approximately 10% shell-wall material. The level of fragrance added to the product was 0.8%, and leaching was followed by headspace measurement via Solid Phase Microextraction (SPME).

As can be seen from Figure 3, after storage at ambient temperature for six weeks, the release of fragrance materials is inversely related to log P.

The fragrance used in Examples 1 and 2 above was comprised of equal weight percents of the following fragrance materials:

Ethyl-2-methyl valerate (manzanate); limonene, DH myrcenol, phenyl ethyl alcohol, benzyl acetate, geraniol, dimethyl benzyl carbonate acetate, methyl nonyl acetaldehyde, cyclacet, methoxy naphthalene (yara yara), beta ionone, lilial, hexyl salicylate and tonalid.

EXAMPLE 3

A slurry of capsules having shell walls composed of an acrylamide-acrylic acid co-polymer cross-linked with melamine-formaldehyde resin was mixed with a commercially obtained concentrated fabric conditioner (DOWNY, Procter & Gamble). The capsules slurry contained fragrance levels as noted below, and approximately 10% shell-wall material. The level of fragrance added to the product was 0.8%, and leaching was followed by headspace measurement via Solid Phase Microextraction (SPME). The fragrance used consisted of either Lilial (logP = 4.4, slurry level = 14%) or Cyclacet (logP = 3.3, slurry level = 24%).

DOWNY (Procter & Gamble, Cincinnati, Ohio) fragrance fabric softener was purchased from a local grocery store and contained approximately 25% cationic surfactants as the active. As can be seen from the table below, after storage at ambient temperature, for up to five weeks at ambient temperature, the released level of Lilial was low and relatively constant, while that of Cyclacet was high and increasing.

	% Free fragrance		
	1 week	2 weeks	5 weeks
Lilial capsule	3	2	12
Cyclacet capsule	62	72	87

EXAMPLE 4

A slurry of capsules having shell walls composed of an acrylamide-acrylic acid co-polymer cross-linked with melamine-formaldehyde resin made as described above was mixed with a model shampoo base. The capsule slurry contained fragrance levels as noted below, and approximately 10% shell-wall material. The level of fragrance added to the product was 0.8%, and leaching was followed by headspace measurement via Solid Phase Microextraction (SPME). The fragrance used consisted of either Lilial (logP = 4.4, slurry level = 14%) or Cyclacet (logP = 3.3, slurry level = 24%).

The shampoo base had an anionic surfactant as the main active with a concentration of 10% and contained sodium laureth (3) sulfate.

Other ingredients in the shampoo included Cocoamido propyl betaine, MEA amides, solvents, conditioning agents (silicone, cationic polymer, etc), etc.

As can be seen from the table below, after storage at ambient temperature for up to six weeks at ambient temperature, the released level of Lilial was low and relatively constant, while that of Cyclacet was high and increased over time.

Shampoo Base		1 week	3 weeks	6 weeks
Lilial		5	7	14
Cyclacet		32	105	91

This Example demonstrates that despite the different bases and different nature of the ingredients in each base in Examples 3 and 4, the Lilial capsule was consistently better than the Cyclacet capsule.

EXAMPLE 5

A slurry of NEOBEE M5 oil [Stephan Company, Northfield, IL]- containing capsules (35% level) having shell walls composed of an acrylamide-acrylic acid copolymer cross-linked with melamine-formaldehyde resin was mixed with a fabric softener base containing 0.2% of a model fragrance accord. A lab made fabric softener base was used which contained approximately 9% quaternary amine as the primary active. The slurry was not added to the control product. Both samples were adjusted to have the same concentration of fabric softener actives. The level of Neobee M5 used (encapsulated) in the base was 5%. The two samples were aged for 2 weeks at 40°C and then used to rinse cloth swatches in an identical lab bench test. The fabrics were air dried and the headspace of an equal mass of fabrics were analyzed before and after stirring with steel ball bearings to rupture intact capsules.

	CONTROL		CAPSULES	
	Unstirred	Stirred	Unstirred	Stirred
Headspace	14	36	115	838
Ratio Stirred/Unstirred	-	3	-	7

Clearly, the presence of capsules enhanced the headspace both before and after capsule rupture. More importantly, because the fragrance was stored inside the capsule, approximately 7 times the headspace was observed after stirring than before stirring with the capsule containing experiment, while the Control with neat fragrance increased only 3 times from a much lower unstirred measurement.

The fabrics were also evaluated via benchtop sensory. The fabric odor of those treated with capsules was clearly more noticeable and stronger than the Control, from which fragrance was not noticeable. This example demonstrates that the capsules with the NEOBEE M5 oil absorbed and held the fragrance within the capsule. This clearly demonstrates the ability to shift from fragrance leaching to fragrance absorption into the capsule with proper core design and level of use.

EXAMPLE 6

The following data illustrate how the core solvent and its level affect the performance of capsules.

Three capsules samples were made with 20%, 50% and 80%, respectively, NEOBEE M5 oil inside the capsule while the remaining portion (80%, 50% and 20%, respectively) was an IFF commercially sold fragrance fabric softener fragrance. A capsule containing 20% by weight di-isodecyl adipate and 80 weight percent of the same fragrance in the core was also prepared.

Each of the capsule samples and a neat fragrance (control) were used as the sole fragrance source in a sample of fabric softener. A lab made fabric softener base was used which contained approximately 9% quaternary amine as the primary active. All samples had the same level of added fragrance. The four samples were aged at 37°C for 2 weeks and then used to rinse cloth swatches in an identical lab bench test. The fabrics were air dried and the headspace of an equal mass of fabrics were analyzed before and after stirring with steel ball bearings to rupture intact capsules. The higher the headspace, the better the performance.

The data below shows that as the level of oil is increased from zero to 80%, the headspace increased dramatically, strongly supporting the point that the solvents help stabilize the fragrance inside by reducing fragrance leaching from the capsule and allowing fragrance to be stored in the capsules.

While using a solvent called “DIDA” @ 20% (diisodecyl adipate), the headspace concentration was only 1236, much lower than the 2985 headspace concentration from NEOBEE M5 at the same 20% level. This indicates that solvent selection is also important to achieve stability.

NEOBEE %	Stirred HeadSpace 2 wks @ 37°C
Control	281
20%	2985
50%	4946
80%	8611
20% NEOBEE M5	2985
20% DIDA	1236